Research Article

Oleic acid/oleylamine pair – selective reagent for resizing of lead chalcogenide colloidal quantum dots

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Abstract. Resizing of lead chalcogenide colloidal quantum dots (CQD) could serve as an alternative approach for the preparation of smaller CQDs from larger one. Herein, we report that all non-radioactive lead chalcogenide CQDs namely PbS, PbSe and PbTe undergo resizing by action of oleylamine/oleic acid mixture. Oleylamine/oleic acid pair etch the surface of nanoparticles resulting in the shrinking of their size and changing optical properties. This reagent is selective to lead chalcogenides and doesn't react with cadmium or mercury chalcogenides. The rate of this transformation could be adjusted by varying the amount of reagent. Solvent effects on the resizing of both lead selenide and sulfide was studied. The reaction of lead selenide in contrast to sulfide is very fast. The preparative resizing of lead selenide could be performed by addition of certain amount of reagent followed by the immediate isolation of lead selenide nanocrystals.

Keywords: colloidal quantum dots, resizing, etching, chalcogenides, oleylamine.

1 Introduction

Colloidal quantum dots (CQDs) received the considerable attention due to their potential in electronic and optical applications. Recent Nobel Prize in chemistry 2023 for colloidal quantum dots is the best acknowledgement of the importance of these nanomaterials. Colloidal nanocrystals based on cadmium selenide CQDs are the most developed materials with some practical applications like QLED displays[1-4].

Quantum dots based on the lead chalcogenides represent the materials with auspicious properties for the applications in near-infrared spectral range. All lead chalcogenides PbS, PbSe and PbTe possess large Bohr exciton radius (from 18 nm to 150 nm) and band gap in bulk (0.28 - 0.41 eV) and therefore attractive material for the production of colloidal nanocrystals for devices operating in near-IR. Known PbS colloidal QDs exhibit absorption peaks at the range from 800 nm to 2100 nm and band gap from 0.6 up to 1.7 eV [5]. PbSe colloidal QDs are interesting for SWIR/mid-IR applications since the nanocrystals with first absorption peaks at the range from 900 to 3000 nm are available [6].

The properties of these chalcogenide nanomaterials allow the creation of thin films for the detection in near-infrared and applications in solar cells. Indeed high performance infrared camera sensors based on the lead sulfide CQDs were commercialized very recently [7]. High definition 2.1 MP cameras were manufactured applying PbS based photodiodes for the direct conversion of photons of incident light into electrons.

Lead chalcogenide QDs is the nanomaterial of interest for the construction of solar cells. Since the half of the solar energy reaching the Earth's surface lies in the infrared, that makes solar cells that harvest wavelengths beyond 1 μm attractive solution [8,9]. The solar cells based on the PbS colloidal QDs reached 15.45 % power conversion efficiency recently [10]. Application of PbS QDs for bioimaging in the second biological NIR window is another important application area [11].

The development of the perfect synthesis of lead sulfide QDs with narrow size distribution and good stability was in the focus of the research in the past decades [12,13]. The most common approaches based on the two component synthesis by hot-injection method [14,15]. Unusual morphologies of chalcogenide nanocrystals could be accessed by application of cation exchange from other nanocrystals as starting materials [16,17]. Several efficient methods for the production of PbS QDs by decomposition of single precursor were published very recently [18,19]. In general, it is rather difficult to get the broad range of nanocrystals sizes and the narrow size distribution by a single method of PbS synthesis. It should be noted that the dominating hot-injection method requires also an inert atmosphere.

The preparation of larger colloidal QD from smaller QDs by is quite common method, the opposite approach is little studied. Lead chalcogenides colloidal QDs like PbSe or PbS could undergo slow oxidative blue shift due to a shrinking [20,21].

Some examples of cadmium chalcogenide colloidal QDs (CdTe, CdSe) resizing by etching are known. Liu et al. reported that nitrosonium tetrafluoroborate ($NOBF_4$) in-duces the resizing of CdTe QDs by oxidative etching [22]. The resizing of CdSe induced by amines was reported in paper from Li et al. [23]. Etching of PbSe QDs with sodium hydroxide results in formation of hierarchical superstructures.[24] The uncontrolled resizing (aging) of colloidal CQDs due to the oxidative etching considered generally as an undesired process [25].

Nevertheless, the resizing itself could be an attractive opportunity to utilize larger QDs as a starting material for smaller ones. For practical applications it is foremost important to have an option to stop the chemical transformation at the desired moment.

Occasionally we discovered etching of lead sulfide nanoparticles by oleylamine/oleic acid mixture in 2019.[26] Based on this finding we developed the controlled aging method for the simple preparation of colloidal quantum dots of lead sulfide. The method is highly attractive due to the minimum requirements to the lab equipment. Herein we report the expansion of this method to the other lead chalcogenide quantum dots. We demonstrate the utility of this mixture for resizing of lead selenide and telluride.

Herein we report the expansion of this method to other lead chalcogenide quantum dots and investigation of the selectivity of this etching reagent to other nanocrystals. Our new procedure allows to follow up this transformation for lead chalcogenides in a simple way even by performing the reaction in a quartz cell of spectrophotometer. Our finding greatly simplifies the optimization of etching transformation for practical applications. We demonstrate the utility of this mixture for resizing of lead selenide and telluride.

The reaction medium is the way to control the rate and outcome of the chemical transformation. Therefore, detailed study of solvent effects for the first time for lead sulfide CQDs and lead selenides is conducted. The investigation of the etching of lead chalcogenides by various ratios of oleylamine and oleic acid in various solvents and at the different oleylamine/oleic acid ratios is provided.

2   Materials and Methods

Chemicals

Following solvents and chemicals were used without additional purification: lead chloride (99.99%, Acros), sulfur (99.999 %, Acros), oleic acid (90 %, Aldrich), octadecene-1 (90 %, Aldrich), n-hexane (99 % HPLC grade, Macron Fine Chemicals), n-octane (Acros, pure, SLR), tetrachloroethane (Supelco, for spectroscopy), tetrachloromethane and ethanol (96 %, reagent grade, Khimmed). Oleylamine(80–90%, Acros) was dried at 110 °C at reduced pressure (5 mbar) for 2 h. Lead telluride nanocrystals were prepared according to the literature procedure.[27] PbSe nanocrystals were obtained by literature procedure.[9]

Characterization

The optical properties of as-synthesized PbS NCs were studied by ultraviolet/visible (UV-Vis) NIR spectroscopy. The UV-Vis spectra were recorded over 200–2500 nm using a UV-Vis-NIR spectrophotometer (V-770, JASCO). The crystal structure was identified by X-ray diffraction (XRD) (ARL X'TRA Xray powder diffractometer, Thermo Fisher Scientific Inc.) using CuKα radiation. The chemical compositions were explored by X-ray photoelectron microscopy (XPS, PHOIBOS 150 MCD, Specs) using Mg Kα radiation (1253.6 eV) and Fourier transform infrared spectroscopy (FT-IR) (Spectrum 100, Perkin Elmer). ^{1}H NMR Spectra were recorded using a 500 MHz Varian Unity Inova Spectrometer. Chemical shifts (ppm) are given relative to solvent. The morphological and structural features of the synthesized nanoparticles were investigated by a transmission electron microscope (TEM, JEM-2100, JEOL).

General procedure for the PbS QDs resizing study

0.1 ml of OA/OLA 1:1 mixture in TCE was added to the 2 ml PbS QDs solution (5 mg/mL) in the spectrophotometer 10 mm quartz cell. The reaction mixture was stored at room temperature for 2 hours and spectra were recorded in certain time intervals.

General procedure for the PbSe QDs resizing study

0.1 ml of OA/OLA 1:1 mixture in TCE was added to the 2 ml PbSe QDs solution (5 mg/mL) in the spectrophotometer 10 mm quartz cell. The reaction mixture was stored at room temperature for 2 hours and spectra were recorded in certain time intervals.

3 Results and Discussion

3.1 The measurement of the etching kinetics for lead chalcogenides. Method development.

The resizing of the lead chalcogenides nanocrystals in the presence of oleylamine/oleic acid mixture is reversed process to the formation of the lead chalcogenides by hot-injection synthesis. The process involves slow dissolution of semiconductor nanocrystal surface by oleylamine/oleic acid. By addition of a large excess of resizing reagent, the chalcogenide nanocrystals could be dissolved completely at room temperature forming a clear solution of a mixture of lead oleate and oleylammonium hydroselenide or hydrosulfide.

$$PbSe_{NC} + [C_{18}H_{35}NH_3^+]C_{17}H_{33}COO^- \longrightarrow Pb(OOCC_{17}H_{33})_2 + [C_{18}H_{35}NH_3^+]HSe^-$$

To follow up this process spectrophotometry could be used. It is always two options for the size estimation of colloidal quantum dots in solution. First and the direct one is calculation based on the band gap estimated from absorption spectra by Tauc method.[28] Second option is available for the solutions with known concentration. According to the equation that is developed by Moreels at al. [5] for PbS nanoparticles the molar extinction at 400 nm depends on the diameter of nanoparticles (d).

$$\varepsilon_{PbS,400} = (0.0233 \pm 0.0001)d^3 \; cm^{-1}/\mu M$$

The absorption of colloidal solution at this wavelength changes according to the Beer–Lambert–Bouguer law and will be $A_{400} = \varepsilon_{400} *c*l$. It means, that the optical density of diluted colloidal solution at 400 nm will depend on the size of nanocrystals PbZ (S,Se) in colloidal solution during the resizing.

$$D_{400} \sim A_{400} \sim d^3$$

The similar equation for molar extinction at 400 nm reported by Moreels et al for spherical lead selenide nanoparticles. [6]

$$\varepsilon_{PbSe,400} = (0.0277 \pm 0.0005)d^3 \; cm^{-1}/\mu M$$

This option is more attractive for the measurement of etching kinetics since the absorption spectra of lead chalcogenides possess exitonic absorption peaks in the range between 1000-2000 nm. Hydrocarbon solvents these are applied for the transformation possess strong absorption in the same range. That makes estimation of the band gap due to the overlapping with hydrocarbon solvents in many cases impossible. (Fig 1.)
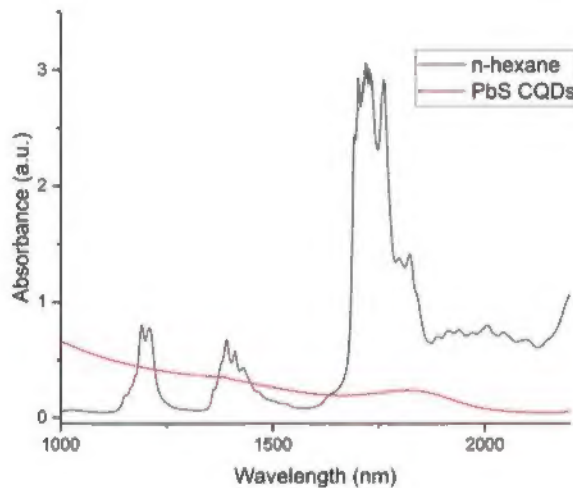

Fig. 1. Absorption spectra of hexane (red) and PbSe colloidal solution in TCE.

Nevertheless if the concentration of quantum dots in solution doesn't change during the process then absorption at 400 nm depends on the size of nanocystals in colloidal solution. The analysis of size distribution diagrams of PbS CQDs during the resizing was reported by us earlier. [26] This analysis demonstrated that the concentration of

quantum dots in solution doesn't change during the process. Careful examination of TEM images from large areas revealed that ratio between large and small PbS quantum dots doesn't change. Only the size of quantum dots decreases during the process.

Based on these observation for PbS and PbSe quantum dots we developed the procedure for the investigation of quantum dots shrinking in the presence of oleylamine/oleic acid mixture. It was found that in some solvents continuous light irradiation of the sample during the spectra measurement could accelerate the dissolution of nanoparticles. Therefore, spectra were measured by certain time intervals and not continuously. Example of absorption spectra development for lead sulfide quantum dots during the resizing in *n*-hexane in the presence of various amounts of oleylamine/oleic acid mixture is depicted on the Fig. 2.
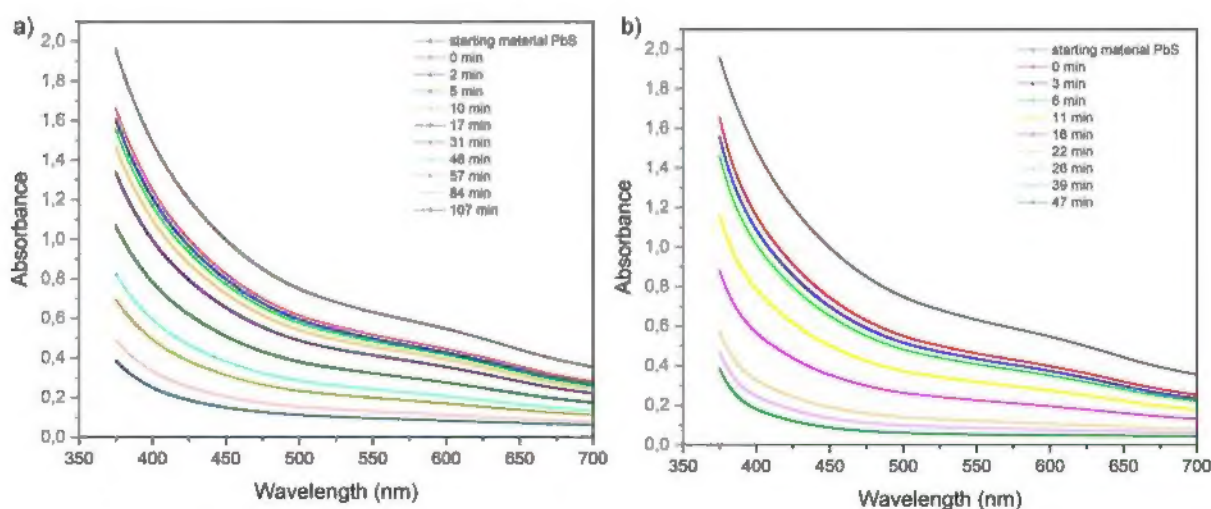

Fig. 2. Development of absorbance of PbS QDs colloidal solution at 400 nm in the presence of OA/OLA reagent in *n*-hexane. a) 0.1 ml; b) 0.3 ml.

Analysis of the data revealed that reaction proceeds very fast within the first minute of experiment. The significant decrease of optical density after an addition of oleylamine/oleic acid mixture was observed. The exact the magnitude of decrease in optical density depends on the amount of reagent applied (Fig. 3). Within next 20 minutes it proceeds linear with reaction rate depended on the amount of reagent.
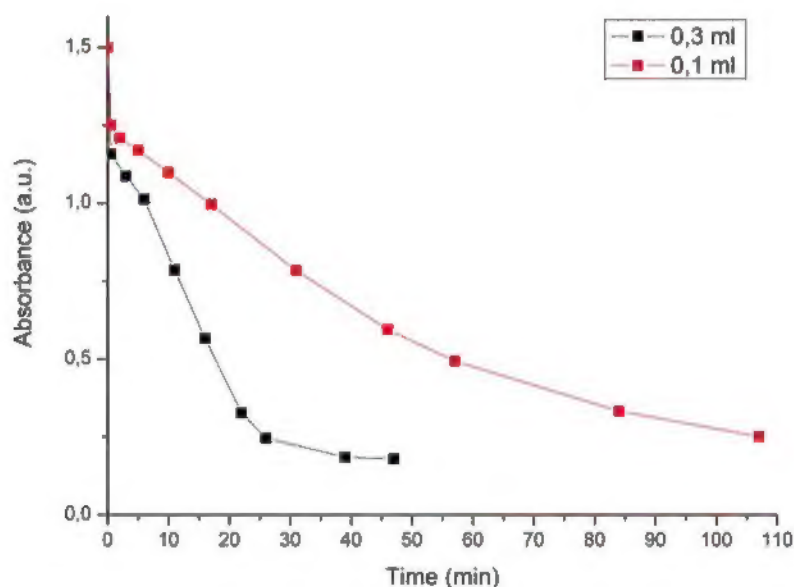

Fig. 3. Development of absorbance of PbS QDs colloidal solution at 400 nm in the presence of OA/OLA reagent in *n*-octane.

Both solvent effect as well as impact of the constitution of resizing reagent were studied. The reaction medium makes significant impact on the rate of the transformation. Several aprotic non-polar solvents namely *n*-hexane, *n*-octane, 1-octadecene, tetrachloromethane and tetrachloroethylene were tested as a reaction medium. These solvents have different polarity and viscosity (Table 1). These two parameters could have impact on the studied transformation. [29,30] The highest reaction rate among all tested solvents was observed in the octane. This transformation proceeds slow in tetrachloromethane (Fig. 4).
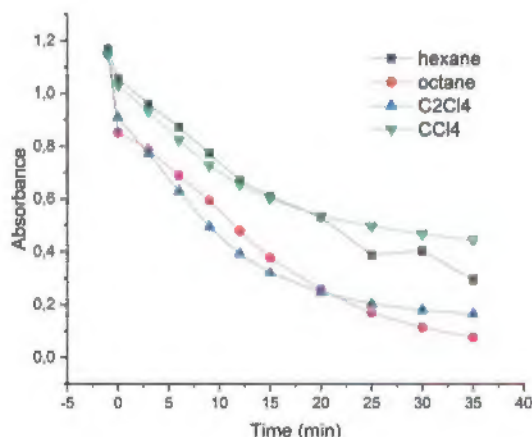

Fig. 4. Development of absorbance of PbS QDs colloidal solution at 400 nm in the presence of 0.3 ml OA/OLA reagent in various solvents.

Table 1. Properties of solvents.

Solvent	Boiling point [°C]	Relative polarity[31] E_N^T	Dynamic viscosity[32] (cP)
n-hexane	69	0.009	0.297
n-octane	125	0.012	0.51
octadecene	315	not available (0.052)[1]	2.7
tetrachloromethane	76	0.052	0.91
tetrachloroethylene	121	0.043	0.89

[1] relative polarity of the n-hexene.

In case of 1-octadecene as a solvent photoassisted dissolution of nanoparticles was observed. The cell with investigated mixture of PbS CQDs and resizing reagent during the measurement of adsorption spectra in UV-range transforms into the two layered system: transparent lower one and black upper with CQDs one. Transparent solution indicates complete dissolution of lead sulfide. That doesn't happen without light irradiation by storing in this solvent. Mixing of two layers and following measurement lead to the formation of the similar two layered system. The position of transparent layer is always on the same level as a light pass in the cell.

Oleic acid or oleylamine alone doesn't induce the resizing of lead sulfide on the significant rate. Only the mixture of oleylamine with oleic acid trigger the shrinking of the lead sulfide quantum dots efficiently. We studied impact of the excess of the oleylamine or oleic acid on the resizing process. Resizing was studied in the presence of oleylamine/oleic acid mixtures in the ratio from 2:1 to 1:2 at room temperature (Fig. 5). It was found that this ratio doesn't have any significant impact on the rate of the transformation.
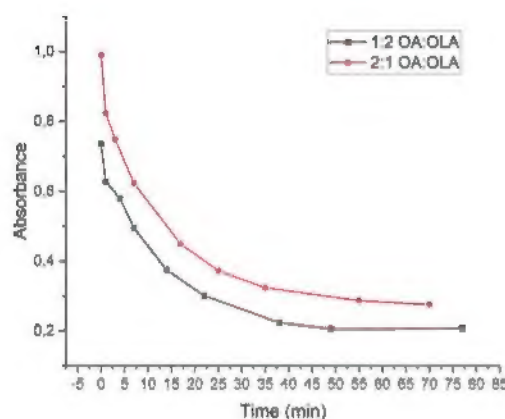
Fig. 5. Development of absorbance of PbS QDs colloidal solution at 400 nm in the presence of 0.3 ml OA/OLA reagent by various OLA:OA ratios.

3.2 PbSe CQDs resizing

Similar to the lead sulfide the lead selenide nanoparticles dissolve in the oleic acid/oleylamine mixture. Action of oleic acid/oleylamine mixture on the PbSe nanoparticles was never investigated in detail before.

PbSe CQDs were obtained by procedure of Liu et al. applying TOPSe as selenium source.[9] PbSe CQDs of mean diameter of 7.5 nm were stored in hexane before use (Fig.6 a-b). The applied colloidal nanocrystals possess crystal structure of clausthalite these remained unaffected by resizing process (Fig. 6c). PbSe CQDs were transferred in desired solvent by blowing the hexane with argon at room temperature and dissolving the sample in equal amount of solvent to restore the concentration.
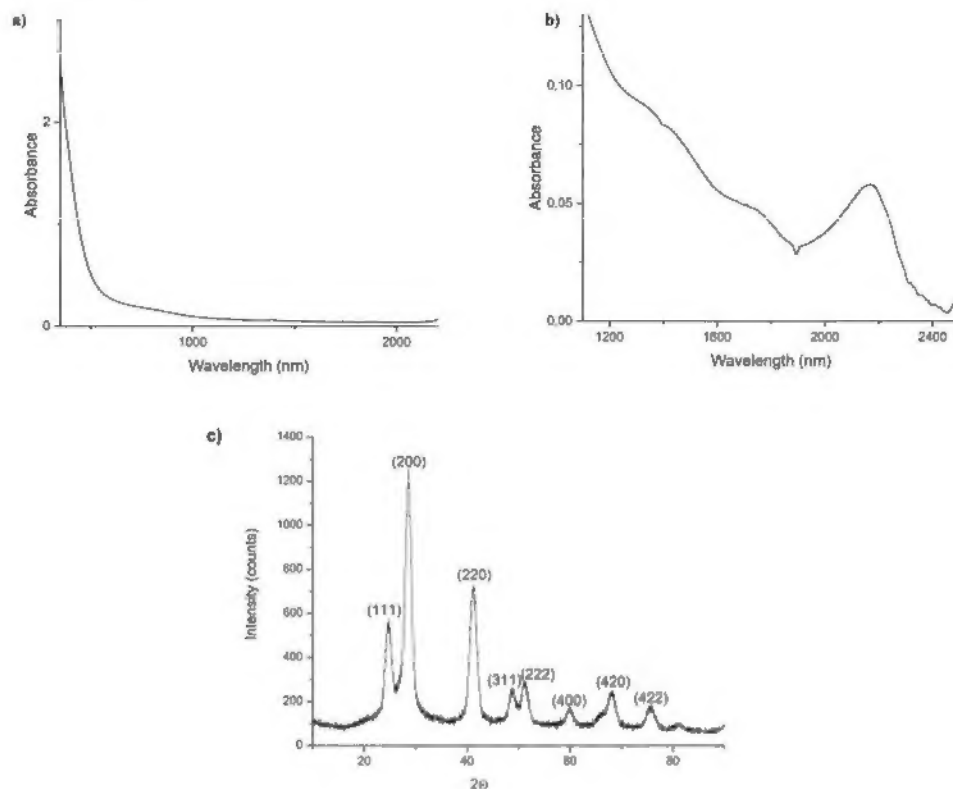

Fig. 6. Absorption spectra of PbSe CQDs in tetrachloroethylene a) 350-2500 nm range, b) 1100-2500 nm range, c) XRD spectrum.

The analysis of size distribution diagrams of PbSe CQDs during the resizing was performed in order to demonstrate that the concentration of quantum dots in solution doesn't change during the process and our method could be extended to PbSe. Indeed, analysis of size distribution diagrams obtained by analysis of TEM images from large areas

demonstrates that ratio between large and small PbSe quantum dots doesn't change. Only the size of quantum dots decreases during the process. Fig. 7a,b depicts TEM image and histogram of 7.5 nm mean size PbSe quantum dots. Fig. 7c,d depicts TEM image and histogram of 6.5 nm mean size PbSe quantum dots after resizing. These images provide evidence that resizing process by oleylamine/oleic acid solution simply «shifts» the size-distribution curve to the smaller sizes. This hypothesis is confirmed by the evaluation of concentration from the known starting and resulting sizes of nanoparticles after isolation of material measured by TEM.
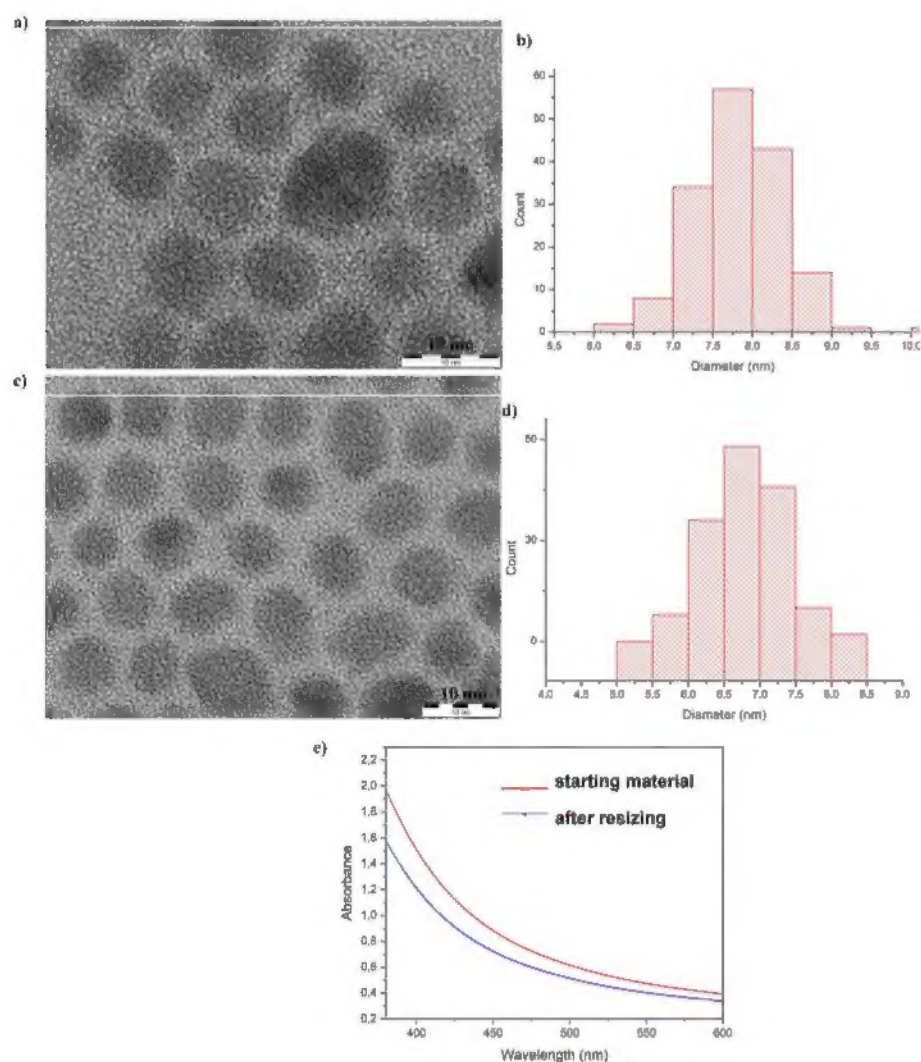

Fig. 7. a) TEM Image of PbSe CQDs before etching; b) Size-distribution histogram before etching, c) TEM Image of PbSe CQDs after etching; d) Size-distribution histogram after etching, e) absorption spectra of quantum dots before and after resizing

Our preliminary studies revealed that resizing of lead selenide QDs in hexane proceeds very fast at room temperature even with smallest amounts of OA/OLA mixture. Several attempts were done in order to perform the transformation for PbSe in controllable manner like the «aging» of lead sulfide QDs.

First at all, solvent effect was studied. The reaction medium could make a significant impact on the reaction rate. The similar row as for PbS QDs of aprotic non-polar solvents were tested (n-hexane, n-octane, 1-octadecene, CCl_4, C_2Cl_4) as a reaction medium. It was found that in case of PbSe CQDs significant change of optical density and therefore size of nanoparticles take place within first two seconds (Fig. 8 a,b) . The exact value of this drop depends on the amount of reagent. There is no change in optical density was observed in the next 20 minutes in all cases. That means that for all tested concentrations of OA/OLA reagent in all tested solvents reaction time was below 2 seconds. The solvent properties for selected media like polarity and viscosity doesn't influence the initial drop of the optical density. The reaction time is below time of absorption spectra recording with spectrophotometer and make the analysis of reactions kinetics in this case impossible.
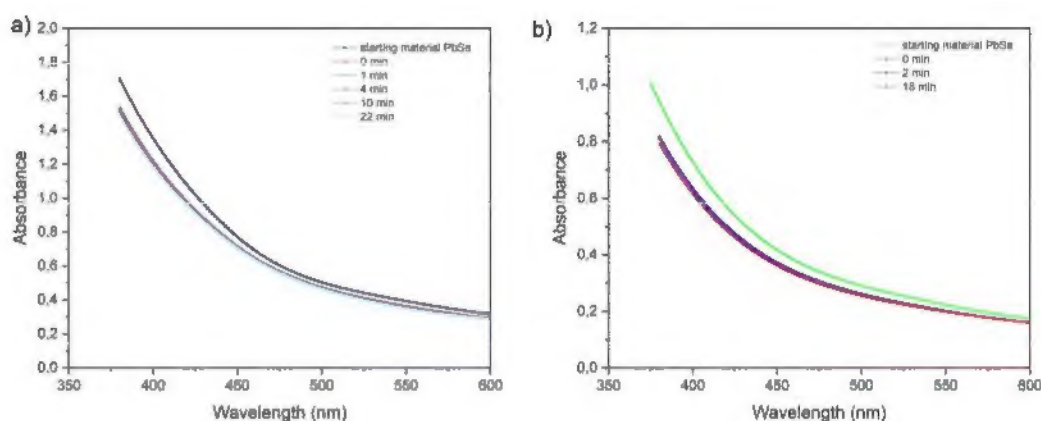
Fig. 8. Development of the PbSe QDs absorption spectra in UV-vis range (380-600 nm) in the presence of OA/OLA reagent: a) octane; b) CCl4.

Even dilution of the added OLA/OA solution by 100 times or adding smaller amounts doesn't change the rate of resizing. The amount of the added reagent influence only the initial drop of optical density.

Adjustment of solvent, concentration and amount of reagent are typically used for controlling the rate of transformations (Figure 6). An addition of chemical, serving as decelerator, could be another option for the decreasing reaction rate. The addition of the 1-dodecanthiol is one of such compounds. This reagent acts as a decelerator of crystal growth in the formation of the PbS CQDs and allows to synthesize the ultrasmall PbS quantum dots [33]. The nature of the deceleration of the crystal growth is due to the strong coordination on the nanocrystal nuclear. In our case the addition of 1-dodecanthiol resulted in the agglomeration of CQDs and precipitation of lead selenide in form of large aggregates from the solution. It was observed as a growth of optical density in the full spectral range due to the growing scattering.

The development of the absorption spectra of PbS CQDs during the aging in the presence of oleylamine-oleic acid mixture.

Nevertheless, the resizing procedure for lead selenide could be performed by addition of certain amount of reagent followed by the immediate isolation of lead selenide nanocrystals.

We found that absorption spectra of lead telluride CQDs solutions in octane undergo the same changes in the presence of oleylamine/oleic acid mixture as other lead chalcogenides namely PbS and PbSe. It is clear indication of resizing of PbTe nanoparticles. By prolonged period of time with large excess of resizing reagent dark colloidal solution transforms into the transparent one of lead oleate. Lead telluride suspensions are very sensitive to the oxygen of air and easily oxidized. We failed to isolate unoxidized samples of lead telluride on open air. This make the resizing procedure for lead telluride unattractive due to the necessity of inert atmosphere for the transformation and later isolation.

Additional experiments with several chalcogenides like mercury sulfide and mercury selenide CQDs as well as Bi2Te3 nanosheets revealed that this transformation is lead chalcogenides specific (Fig. S1-S2). Both HgS and HgSe are not affected by the resizing reagent in hydrocarbons even at the highest concentration of OLA/OA mixture in the reaction mixture. Bi2Te3 nanosheets do not change in the presence of this reagent as well.

4 Conclusions

It was found that all non-radioactive lead chalcogenide CQDs namely PbS, PbSe and PbTe could react with oleylamine/oleic acid mixture. The result of this reaction is shrinking of the semiconductor core and resizing of nanoparticles. The rate of transformation could be performed by monitoring of absorption changes at 400 nm by spectrophotometry for any colloidal solution of PbZ (S/Se/Te) nanoparticles. The rate of resizing depends on the chalcogenide. Lead selenide reacts much faster than lead sulfide. Only resizing of lead sulfide could be performed in time-controllable manner as « the controlled aging». The rate of this transformation could be adjusted by varying the amount of reagent or solvent. Reaction in octane was fastest for PbS CQDs. The resizing in chlorinated solvent proceeded much slower than in hydrocarbons. The resizing of lead selenide could be performed by addition of certain amount of reagent followed by the immediate isolation of lead selenide nanocrystals. The action of oleylamine/oleic acid reagent is selective to lead chalcogenides, since other tested chalcogenide nanocrystals (CdSe, HgS, HgSe, Bi2Te3) were not affected by this reagent.

Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The corresponding author declares that the paper is submitted in a personal capacity and not as a representative of the Government of the Russian Federation.

The corresponding author confirms that there is no conflict of interest between co-authors.

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